



Environmental and Chemical Aging of Fatty-Acid-Based Vinyl Ester Composites

by Steven E. Boyd and John J. La Scala

ARL-TR-5523

April 2011

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) April 2011		2. REPORT TYPE Final		3. DATES COVERED (From - To) October 2009–September 2010	
4. TITLE AND SUBTITLE Environmental and Chemical Aging of Fatty-Acid-Based Vinyl Ester Composites		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S) Steven E. Boyd and John J. La Scala		5d. PROJECT NUMBER H84			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WMM-B Aberdeen Proving Ground, MD 21005-5069		8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-5523			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT As part of an ongoing validation effort to replace conventional monolithic materials with composite material structures for proposed U.S. Department of Defense applications, environmental and chemical aging was conducted on selected glass-reinforced vinyl ester matrix composites. The composites consisted of two matrices: commercially available vinyl ester resins with styrene contents >40 weight-percent and more environmentally friendly, sustainable vinyl ester resins with methacrylated fatty acids to replace a significant percentage of the hazardous air pollutant (HAP) styrene. Fatty-acid vinyl ester (FAVE) bioresins have a lower weight-percent of styrene (<25 weight-percent) and produce less HAP emissions during processing. They are being investigated to replace higher styrene content vinyl ester resins. This effort's objective was to evaluate the impact of environmental and chemical aging on the mechanical response/properties of glass-reinforced composites with commercially available vinyl ester resins and FAVE bioresins and compare them directly. Although lowering styrene content can cause overall mechanical and thermal properties to decrease slightly, mechanical performance after aging of FAVE biocomposites demonstrated that they are just as resistant to certain environmental and chemical aging as commercially available, higher styrene content vinyl ester resin composites. This study identified no impediment to replacing higher styrene content resins with FAVE bioresins.					
15. SUBJECT TERMS aging, fatty-acid vinyl esters, biocomposites, FAVE bioresins, styrene content					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 32	19a. NAME OF RESPONSIBLE PERSON Steven E. Boyd
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-1927

Contents

List of Figures	iv
List of Tables	v
Acknowledgments	vi
1. Introduction	1
2. Materials and Experimental	3
2.1 Fibers and Resins.....	3
2.2 Composite Manufacture	4
2.3 Mechanical Testing of Composites	4
2.3.1 Dynamic Mechanical Analysis.....	4
2.3.2 Flexural Testing.....	5
2.3.3 Short Beam Shear Testing.....	5
2.4 Environmental and Chemical Aging	6
2.4.1 Determination of Wet and Dry Glass Transition Temperatures.....	7
2.4.2 Cyclic Freeze and Thawing Tests	7
2.4.3 Xenon Arc Lamp Weathering	7
2.4.4 Fluid Aging.....	8
3. Results and Discussion	9
3.1 Flexural Properties	9
3.2 Short Beam Shear.....	14
3.3 Wet and Dry Glass Transition Temperature.....	16
4. Conclusions	18
5. References	19
Distribution List	21

List of Figures

Figure 1. DOD applications for low-HAP composites.	2
Figure 2. ATLAS xenon weathering testing apparatus and schematic of inner chamber.....	8
Figure 3. Normalized flexural strength of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.	10
Figure 4. Normalized flexural strength of aged commercial resin composites vs. their unaged commercial composite counterparts.	11
Figure 5. Normalized flexural stiffness of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.	12
Figure 6. Normalized flexural stiffness of aged commercial resin composites vs. their unaged commercial composite counterparts.....	13
Figure 7. Normalized SBS strength of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.....	14
Figure 8. Normalized SBS strength of aged commercial resin composites versus their unaged commercial composite counterparts	15
Figure 9. Dry and wet glass transition temperatures for commercial and FAVE composites.....	17
Figure 10. Glass transition temperatures (dry) for commercial and FAVE composites: baseline (no aging), JP8 aging, freeze-thaw-soak aging, and MEK aging.	17

List of Tables

Table 1. Proposed applications for commercial vinyl ester and FAVE composites in the U.S. Military.	3
Table 2. Composite lay-up, approximate thickness, and estimated fiber and matrix volume fraction for studied commercial vinyl ester and FAVE composites.	4
Table 3. Relevant aging testing per application and proposed FAVE composite replacement.	6
Table 4. Baseline mechanical and thermal properties for unaged composites with commercially available resin matrices.	9

Acknowledgments

This research was supported in part by an appointment to the Postgraduate Research Participation Program at the U.S. Army Research Laboratory (ARL) administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and ARL.

1. Introduction

Composite materials are used in the U.S. Department of Defense (DOD) because of their low weight and excellent properties, enabling the production of lighter-weight and stronger vehicles, ships, and structures. Programs have been initiated to replace metallic components of the high-mobility, multipurpose, wheeled vehicle (HMMWV) and other U.S. Army vehicles and naval ships with composite parts. Future classes of vehicles and ships will use significantly higher amounts of composite materials, making these vehicles lighter, faster, and more maneuverable. However, aspects of these technologies have an adverse effect on the environment. Fabrication of composite materials produces volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions. Sources of pollution from these materials include disposal of hazardous polymer ingredients, solvents used for viscosity reduction, gases evolved during and after processing, and disposal of contaminated scrap materials (1).

The U.S. Environmental Protection Agency has established regulations limiting the amount of VOCs, HAPs, and heavy metals that can be used in composite materials under the National Emissions Standards for Hazardous Air Pollutants (NESHAP) (2). This regulation established facility-wide emissions limits, which make compliance through low-emissions materials desirable. Reactive diluents in vinyl ester and unsaturated polyester resins, such as styrene and methyl methacrylate, are used to reduce the resin viscosity to enable liquid molding. However, these diluents are VOCs and HAPs and are specifically regulated for use in composite materials under the Reinforced Plastics Composites NESHAP (2). Typical commercial resins contain 40–60-weight-percent styrene. There are some low-HAP varieties that contain as little as 33-weight-percent styrene, such as Derakane 441-400. However, the viscosity and fracture properties of such resins are poor. Therefore, DOD facilities would need to implement add-on control devices to capture volatile emissions from composite processing in order to use the high-performance commercial resins. Considering the number of current and future DOD sites using composite resins, the cost of implementing these add-on facilities is prohibitive (3). The alternatives would be to use more expensive epoxy resins ($\sim 3\times$ more expensive) or to reduce the usage of composites in the DOD, making it difficult to realize the initiative to make a lighter, faster, and more maneuverable military.

A potential solution for manufacturing NESHAP-compliant vinyl ester resins with polymer properties and performance similar to that of commercially available vinyl ester resins has been developed (4). Fatty-acid vinyl esters (FAVEs) use methacrylated fatty-acid monomers, such as methacrylated lauric acid, as reactive diluents to replace all but 10%–25% of the resin styrene content in vinyl ester resins (5). The FAVE resins have similar resin viscosity (4), polymer properties (4), and composite properties (6) relative to commercial vinyl ester resins. Fatty-acid monomers are excellent alternatives to styrene due to their low cost and extremely low volatility.

In addition, fatty acids are renewable resources because they are derived from plant oils. Therefore, not only would the use of fatty-acid monomers reduce HAP emissions in liquid molding resins (7), thereby reducing health and environmental risks, but it also would promote global sustainability.

Validation platforms for proposed FAVE replacement resins for composite parts are illustrated in figure 1. Applications are varied and range across all services of the DOD and therefore are subject to different thermal and mechanical criteria and must maintain good resistance to application of unique corrosion and corrosive elements. A study was undertaken to examine the effects of environmental and chemical aging on the thermal and mechanical performance of these proposed replacement composites. Attention was directed toward distinguishing the performance and properties of commercially available, higher styrene content matrix composites with newly developed low-HAP and low-VOC FAVE matrix composites.

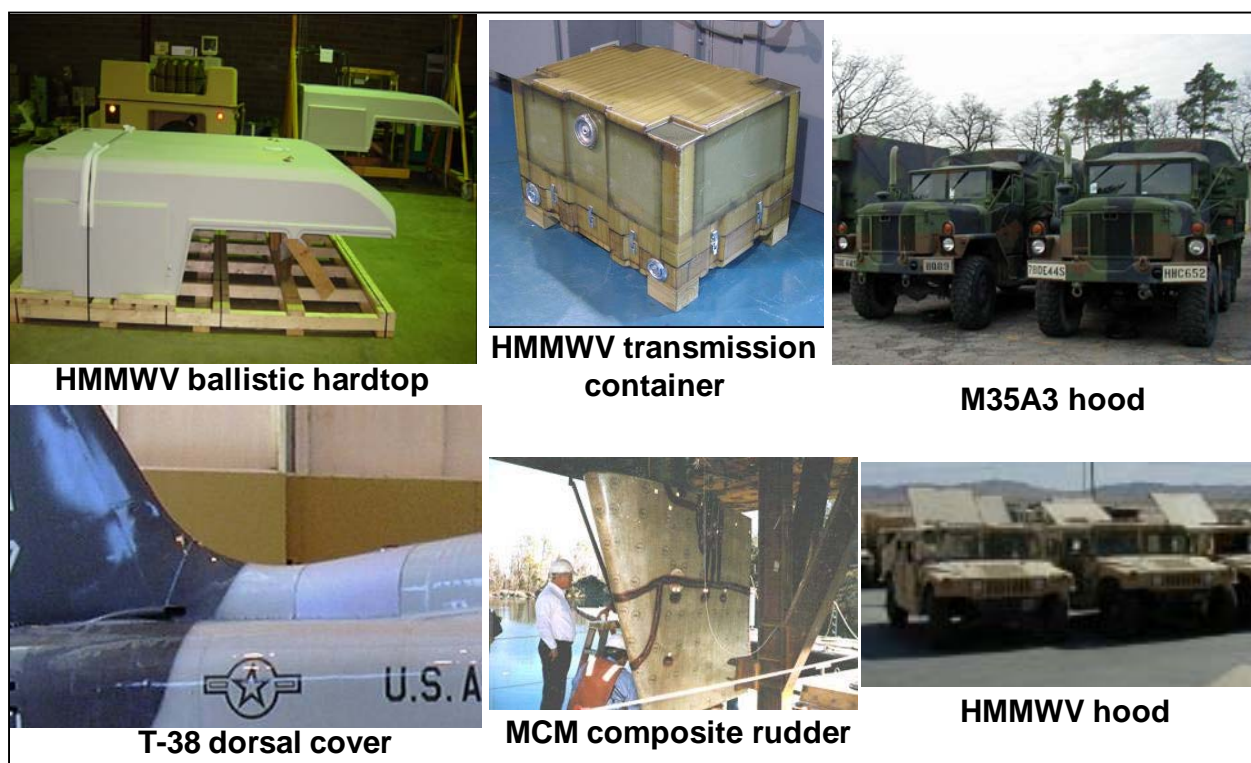


Figure 1. DOD applications for low-HAP composites.

2. Materials and Experimental

2.1 Fibers and Resins

Selection of the fiber and resin systems for a particular DOD application is summarized in table 1. The aging and mechanical testing results of the current study continue the validation procedure for both commercial resins and their proposed low-HAP FAVE replacements. Various U.S. Army applications focus on Derakane 441-400 (higher glass transition temperature T_g with 33-weight-percent styrene) and Derakane 8084 (a rubber-toughened resin with improved fracture-toughness properties and 40-weight-percent styrene) with Mahogany 24-oz/yd² E-glass, 5 × 4, woven roving and 3TEX, Inc., 96-oz/yd² 3WEAVE E-glass with 2022 silane sizing (P3W-GE044). Bioresin replacements for the Derakane resins include FAVE-O-25S (manufactured with methacrylated octanic acid with 25-weight-percent styrene) and FAVE-O-HT (a novolac-based vinyl ester for higher-temperature performance). The U.S. Marine Corps high-mobility, multipurpose, wheeled vehicle (HMMWV) hardtop utilizes 3TEX, Inc., 54-oz/yd² 3WEAVE E-glass with 2022 silane sizing (P3W-GE045) with Derakane 8084 and FAVE-O-25S. The U.S. Air Force application for the T-38 dorsal cover and F-22 canopy cover utilizes both Fibre Glast Developments Corp. Style 120 3-oz/yd² E-glass satin weave and Style 7781 9-oz/yd² E-glass satin-weave fabric with Hexion Specialty Chemicals 781-2140 (with 47-weight-percent styrene). The U.S. Navy application for the composite rudder currently uses Fiber Glass Industries 18-oz/yd² unidirectional E-glass fiber tows with a stitched mat backing and Interplastic Corp. CoREZYN Corve 8100 (with 50-weight-percent styrene) with the proposed replacement resin FAVE-L-25S (manufactured with methacrylated lauric acid with 25-weight-percent styrene).

Table 1. Proposed applications for commercial vinyl ester and FAVE composites in the U.S. Military.

Application	Fabric	Resin	Resin Replacement
Amtech HMMWV hardtop	3TEX 100-oz S2-glass and 24-oz S2-glass	Derakane 8084	FAVE-O-25S
HMMWV hood	3TEX 54-oz E-glass	Hetron 980/35	FAVE-O-HT
M35A3 and M939 hood	3TEX 96-oz E-glass	Hetron 980/35 (VE) or Huntsman 8605 (epoxy)	FAVE-O-HT
Transmission container	3TEX 54-oz E-glass	Derakane 8084	FAVE-O-25S or FAVE-L-25S
T-38 dorsal cover F-22 canopy cover	Fibre Glast Developments Corp. Style 120 3-oz E-glass and Style 7781 9-oz E-glass	Hexion 781-2140	FAVE-L-25S or FAVE-O-25S
MCM rudder	Fiber Glass Industries 18-oz unidirectional stitched mat E-glass	CoREZYN Corve 8100 and Derakane 510A-40	FAVE-L-25S

2.2 Composite Manufacture

Composite panels were manufactured for all 12 composites using vacuum-assisted resin transfer molding to provide samples for testing (8). The chemical cure package used included Condea Servo Cobalt Naphthenate as a catalyst, Akzo Nobel TrigonoX 239A antifoaming organic peroxide as an initiator, EMD N,N-Dimethylaniline as a promoter and wetting agent, and Avocado Research Chemicals Ltd. 2,4-Pentanedione, 99% as an inhibitor. Gel time studies were performed for each resin using various weight-percentages of these chemicals to arrive at a gel time of ~1 h or less. Composite panels were laid up to a thickness required by the thickness-to-width and span ratios set forth in ASTM D 790-03 (9) and ASTM D 2344-00/D 2344M-00 (10), and the panel thickness did not exceed 4 mm for all composites. The lay-ups and approximate thicknesses of the individual composites are listed in table 2.

Table 2. Composite lay-up, approximate thickness, and estimated fiber and matrix volume fraction for studied commercial vinyl ester and FAVE composites.

Composite	Lay-Up	Thickness (mm)	V _f (%)	V _m (%)
3 oz/Hexion	32-ply, warp	~3.5	40.6	59.4
3 oz/FAVE-O-25S	32-ply, warp	~3.8	39.6	60.4
9 oz/Hexion	[0/90]3s	~2.7	50.7	49.3
9 oz/FAVE-O-25S	[0/90]3s	~2.6	59.8	40.2
18 oz/Corve 8100	[0/90]s	~3.5	46.3	53.7
18 oz/FAVE-L-25S	[0/90]s	~3.5	47.1	52.9
24 oz/Derakane 8084	[0/90/0]s	~3.9	53.0	47.0
24 oz/FAVE-O-25S	[0/90/0]s	~3.9	50.0	50.0
54 oz/Derakane 8084	2-ply, warp	~3	51.5	48.5
54 oz/FAVE-O-25S	2-ply, warp	~3	49.0	51.0
96 oz/Derakane 441-400	Single ply	~2.7	48.6	51.4
96 oz/FAVE-O-HT	Single ply	~2.7	47.9	52.1

2.3 Mechanical Testing of Composites

2.3.1 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) testing was used to determine the glass transition temperature T_g and storage and loss modulus. Tests were conducted on a Thermal Analysis Instruments Q800 DMA unit using a dual-cantilever geometry. Samples of dimensions 60×12 mm by the thickness of each individual composite (table 2) were cut, and temperature ramps from 25–200 °C with a constant heating rate of 2 °C/min and constant oscillatory amplitude of 7.5 μ m were performed. In cases of fluid contamination or water sorption, a second temperature ramp was performed immediately after the first without removing the sample from the dual-cantilever grip. T_g is determined as the peak of the loss modulus vs. temperature curve.

2.3.2 Flexural Testing

Basic mechanical performance was assessed through flexural strength and short beam shear (SBS) testing. The standard test for flexural strength, stiffness, and failure strain for reinforced plastics is established in ASTM D 790-03 (9). For the highly orthotropic laminates and three-dimensional (3-D) weave-reinforced composites in this study, a span-to-thickness ratio of at least 40:1 was used, resulting in a sample span of at least 140 mm with an average thickness of 3.5 mm. Crosshead rate was determined from the following equation:

$$R = \left(\frac{ZL^2}{6d} \right) , \quad (1)$$

where R is the crosshead speed, Z is the rate of straining that is constant at 0.01, L is the sample span, and d is the sample thickness. A flexural load is applied in a 3-point bend geometry until rupture occurs in the outer surface of the sample or until a maximum strain of 5% is reached. The flexural modulus of elasticity, E_B , is calculated by the following:

$$E_B = \left(\frac{L^3 m}{4bd^3} \right) , \quad (2)$$

where b is the width of the sample and m is the slope of the linear portion of the load vs. displacement graph. Since the sample span is $>10\times$ the thickness, a correction factor is applied to the flexural stress calculation to account for large deflections. The flexural strength σ_f is now calculated using the following equation:

$$\sigma_f = \left(\frac{3PL}{2bd^2} \right) \left[1 + 6 \left(\frac{D}{L} \right)^2 - 4 \left(\frac{d}{L} \right) \left(\frac{D}{L} \right) \right] , \quad (3)$$

where P is the maximum load and D is the deflection of the crosshead at maximum load. The failure strain ε_f is calculated using the following equation:

$$\varepsilon_f = \left(\frac{6Dd}{L^2} \right) . \quad (4)$$

2.3.3 Short Beam Shear Testing

SBS strength was also calculated according to standard ASTM D 2344-00/D 2344M-00 (10). The sample width was approximately 4 mm, with the span given as $4\times$ the thickness. A flexural load is applied in a 3-point bend geometry until a maximum load is reached. The SBS strength is given by the following equation:

$$F^{SBS} = 0.75 \times \left(\frac{P_{MAX}}{b \times h} \right) , \quad (5)$$

where P_{MAX} is the maximum load and $b \times h$ is the cross-sectional area.

2.4 Environmental and Chemical Aging

Environmental and chemical aging procedures conducted on the various composites were determined based on the anticipated exposure to environmental and chemical agents over the working lifetime of the composite parts (as summarized in table 3). None of the actual aging tests are exact applications of a standard test but instead are based on standard testing methods listed in test method standard MIL-STD-810F (11) and consultation with Environmental Security Technology Certification Program partners. Duration and intensity of the exposure were chosen to demonstrate some decrease in mechanical and thermal properties over the period of aging. Environmental aging was performed on all commercial and FAVE composites and included wet T_g , freeze/thaw cycling, and xenon arc lamp weathering. Chemical aging included exposure to various chemical agents (method 504, Contamination by Fluids [11]) that were selected as a hydrocarbon fuel (JP-8), a solvent (methyl ethyl ketone [MEK]), and saltwater exposure exclusively for the Navy composites.

Table 3. Relevant aging testing per application and proposed FAVE composite replacement.

Applications	Composites	Resin	Replacement Resin	Aging Tests	
HMMWV transmission container (Army)	Mahogany 24-oz E-glass/Derakane 8084	Derakane 8084	FAVE-O-25S	Wet T_g freeze/thaw	Xenon weathering chemical: JP8
HMMWV hood (Army)	24 oz/Derakane 441-400	Derakane 441-400	FAVE-O-25S	Not tested	
M35A3 hood (Army)	3TEX 3-D weave 96 oz/Derakane 441-400	Derakane 441-400	FAVE-O-HT	Wet T_g freeze/thaw	Xenon weathering chemical: JP8
Amtech HMMWV hardtop (Marine Corps)	3TEX 3-D weave 54 oz/Derakane 8084	Derakane 8084	FAVE-O-25S	Wet T_g freeze/thaw	Xenon weathering chemical: JP8
T-38 dorsal cover (Air Force)	Fibre Glast style 120 3-oz E-glass/Hexion 781-2140	Hexion 781-2140	FAVE-O-25S	Wet T_g freeze/thaw	Xenon weathering chemical: MEK
T-38 dorsal cover (Air Force)	Fibre Glast style 7781 9-oz E-glass unistitch mat/Hexion 781-2140	Hexion 781-2140	FAVE-O-25S	Wet T_g freeze/thaw	Xenon weathering chemical: MEK
MCM rudder (Navy)	Fiber Glass Ind. 18-oz E-glass unistitch mat/Corve 8100	CoRESYN Corve 8100 and Derakane 510A-40	FAVE-L-25S	Wet T_g freeze/thaw	Simulated saltwater solution

2.4.1 Determination of Wet and Dry Glass Transition Temperatures

The Army HMMWV, M35A3, and M939 hoods, in addition to the Marine Corps Amtech HMMWV hardtop, are all subject to dry and wet T_g requirements. To determine the wet T_g for the composites, DMA samples were cut for each composite and soaked in distilled, deionized water and filtered using a Barnstead B-pure water purification unit for days until subsequent weighing of the samples demonstrated no further mass increase. The samples were then tested in a TA Instruments DMA Q800 with a dual-cantilever geometry at 1 Hz; the T_g was determined from the peak of the loss modulus curve vs. temperature. Two temperature ramp runs were conducted on the wet T_g samples to ensure that the dry T_g values were recoverable.

2.4.2 Cyclic Freeze and Thawing Tests

Freeze/thaw aging was conducted on DMA and SBS samples of all composites to assess possible effects of cyclic water sorption and freezing on the SBS properties. Typically with water sorption, a degradation of composite strength and stiffness is observed due to the diffusion of water into the glass fiber and its retention at the fiber/matrix interface. Subsequent cycles of water sorption on freezing should weaken the interfacial bonds and inhibit optimum shear transfer between fiber and matrix under loading. Approximately 15 cycles of freezing and thawing were conducted as follows: 24 h of freezing at $-24\text{ }^{\circ}\text{C}$ and 24 h of thawing and water immersion in deionized water. After the freeze/thaw cycles were completed, the samples were dried or thawed and tested for T_g and SBS strength.

2.4.3 Xenon Arc Lamp Weathering

All composites were subject to weathering tests to simulate real exposure conditions that may be encountered upon mission-critical deployments. A xenon lamp weathering instrument (see figure 2) was selected because the xenon arc lamp radiation output most closely simulates average actual sunlight exposure in the ultraviolet and visible region (300–2450 nm). An ATLAS Ci5000 Weather-Ometer was used to subject all composites to a cycle of radiation exposure of $\sim 1.1\text{ kW/m}^2$ for 20 h and darkness for 4 h at a constant temperature of $49\text{ }^{\circ}\text{C}$ with constant relative humidity of 50%. The cycle of radiation exposure is consistent with guidelines recommended in ASTM practices G 151-00 (12) and G 155-05a (13) and was adapted from a suggested cycle of exposure put forth in military standard MIL-STD-810F, method 505.4 (Solar Radiation), procedure II (11). Composite panels from both commercial and FAVE matrix resins were cut to approximately $200 \times 150\text{ mm}$ and weathered for 62 cycles. After aging was completed, each panel was cut into samples for DMA and mechanical testing.

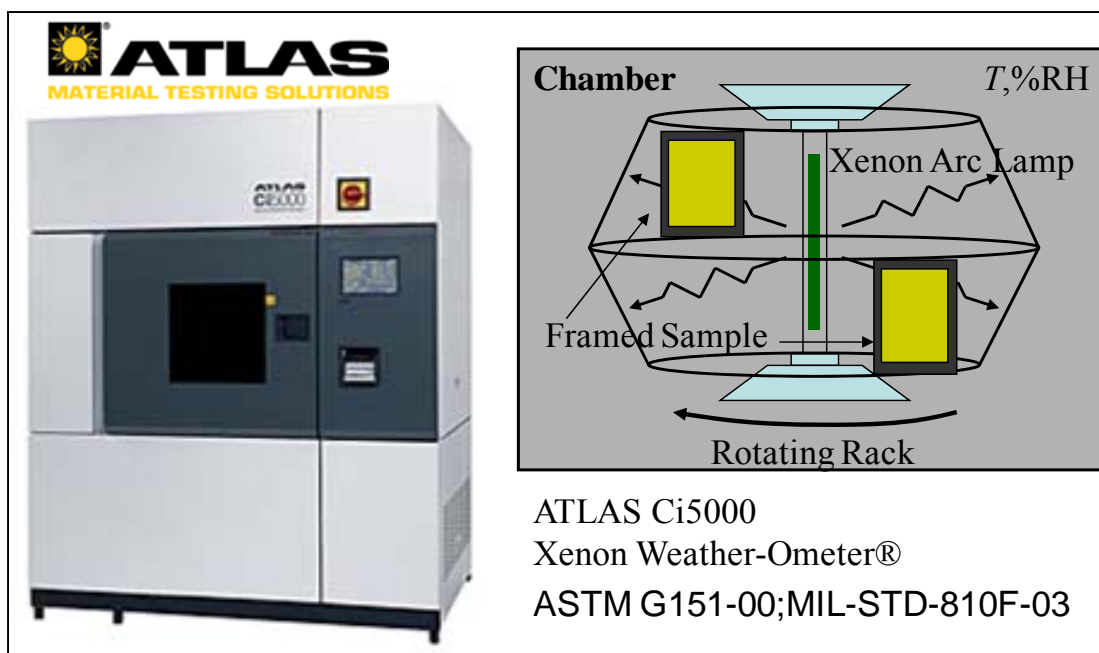


Figure 2. ATLAS xenon weathering testing apparatus and schematic of inner chamber.

2.4.4 Fluid Aging

All composites except the Navy composites (18-oz fabric with either Corve 8100 or FAVE-L-25S) were exposed to hydrocarbon turbine fuel JP-8 (MIL-DTL-83133F [14]) according to military standard MIL-STD-810F, method 504 (Contamination by Fluids) (11). JP-8, of course, is the military standard fuel utilized by all services in multiple combat vehicles. The procedure suggested therein for prolonged exposure was extended from 3 days to 1 week to ensure any possible effect of the JP-8 contamination on the thermal and mechanical properties would be observed. DMA, SBS, and flexural samples were cut from the bulk composite and soaked in a bath of JP-8 at ambient temperature for 1 week and then drained for several days. Drained and fully dried samples were then tested.

All of the Air Force composites, the 3- and 9-oz fabrics with either Hexion 781-2140 or FAVE-O-25S matrices, were exposed to the solvent MEK because it is a widely used industry solvent and a likely reagent that these composites would come in contact with as they are processed and fielded. Alternatively, MEK might simulate other fluids that these materials would come in contact with, such hydraulic fluid. The exact procedure discussed for JP-8 exposure was used, making special note of before and after exposure color changes and leeching into the solvent bath. Drained and fully dried samples were then tested.

The Navy composites, 18-oz fabric with either Corve 8100 or FAVE-L-25S, were exposed to a simulated seawater bath to assess possible corrosion effects on mechanical properties. Cut composite samples were soaked for ~1 month in a solution of 1 liter of VWR distilled water to 40 g of Sigma Aldrich sea salts (S9883). Samples were then dried and tested.

3. Results and Discussion

3.1 Flexural Properties

Flexural strength and stiffness are shown in table 4 and figures 3–6. The difference in flexural strengths and stiffnesses can largely be explained by considering the individual fiber reinforcements. The satin weaves generally had lower strengths, with the 3-oz satin weave having the lowest and the 18-oz unidirectional with stitched mat backing having the highest due to the majority of the fiber reinforcement aligned along the span of bending. The 24-oz plain weave and 3-D weave reinforced composites (96 oz) fell in between due to a nearly 50/50 split in warp/weft fiber reinforcement. The flexural stiffness was understandably lowest for the 3-oz satin weave but fell off for the 3-D weave composites. It is important to note here that sample thickness was constrained to <4 mm by ASTM requirements for most of the mechanical testing performed. As a result, the decision to go with one-layer, 96-oz, 3-D weave reinforcement was forced by testing criteria and, as shown in figures 5-6, had adverse effects on mechanical data illustrated by the 96-oz baseline flexural stiffness in which the sample did not fail by the 5% strain limit.

Table 4. Baseline mechanical and thermal properties for unaged composites with commercially available resin matrices.

Composite	Flex Strength (MPa)	St. Dev.	Flex Stiffness (GPa)	St. Dev.	F ^{SBS} (MPa)	St. Dev.	Dry Tg (C)	Wet Tg (C)
3 oz/Hexion 781-2140	338.9	4.0	17.8	0.1	45.9	1.2	115.0	113.6
9 oz/Hexion 781-2140	636.2	56.2	23.4	1.7	54.0	6.2	116.5	115.3
18 oz/Corve 8100	737.3	54.0	23.3	1.9	33.1	4.2	112.8	107.1
24 oz/Derakane 8084	411.6	29.8	21.1	1.1	37.5	2.0	110.4	107.0
54 oz/Derakane 8084	503.6	52.4	18.7	1.3	34.6	1.0	109.9	103.3
96 oz/Derakane 441-400	498.7	41.7	25.7	1.2	26.5	2.4	121.2	116.5

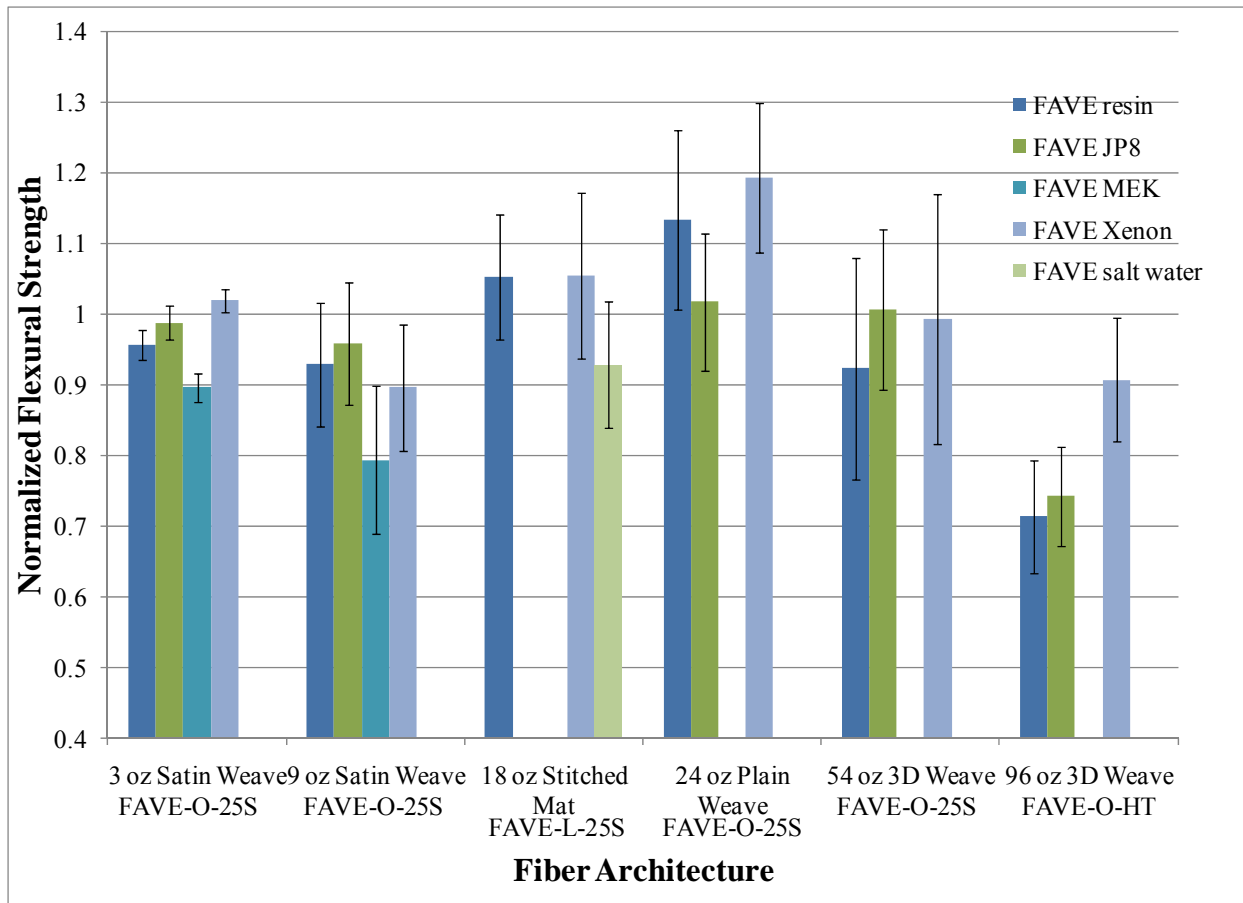


Figure 3. Normalized flexural strength of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.

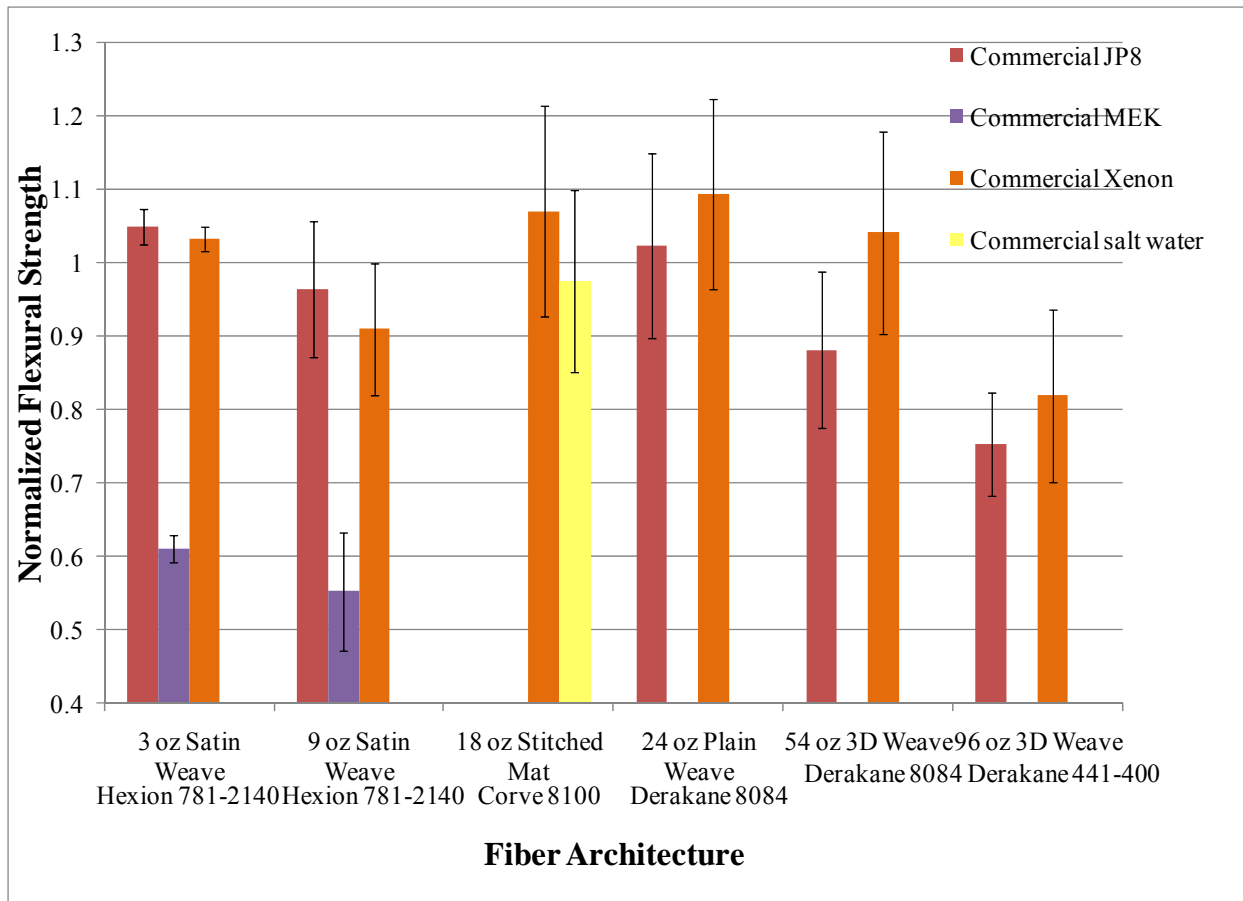


Figure 4. Normalized flexural strength of aged commercial resin composites vs. their unaged commercial composite counterparts.

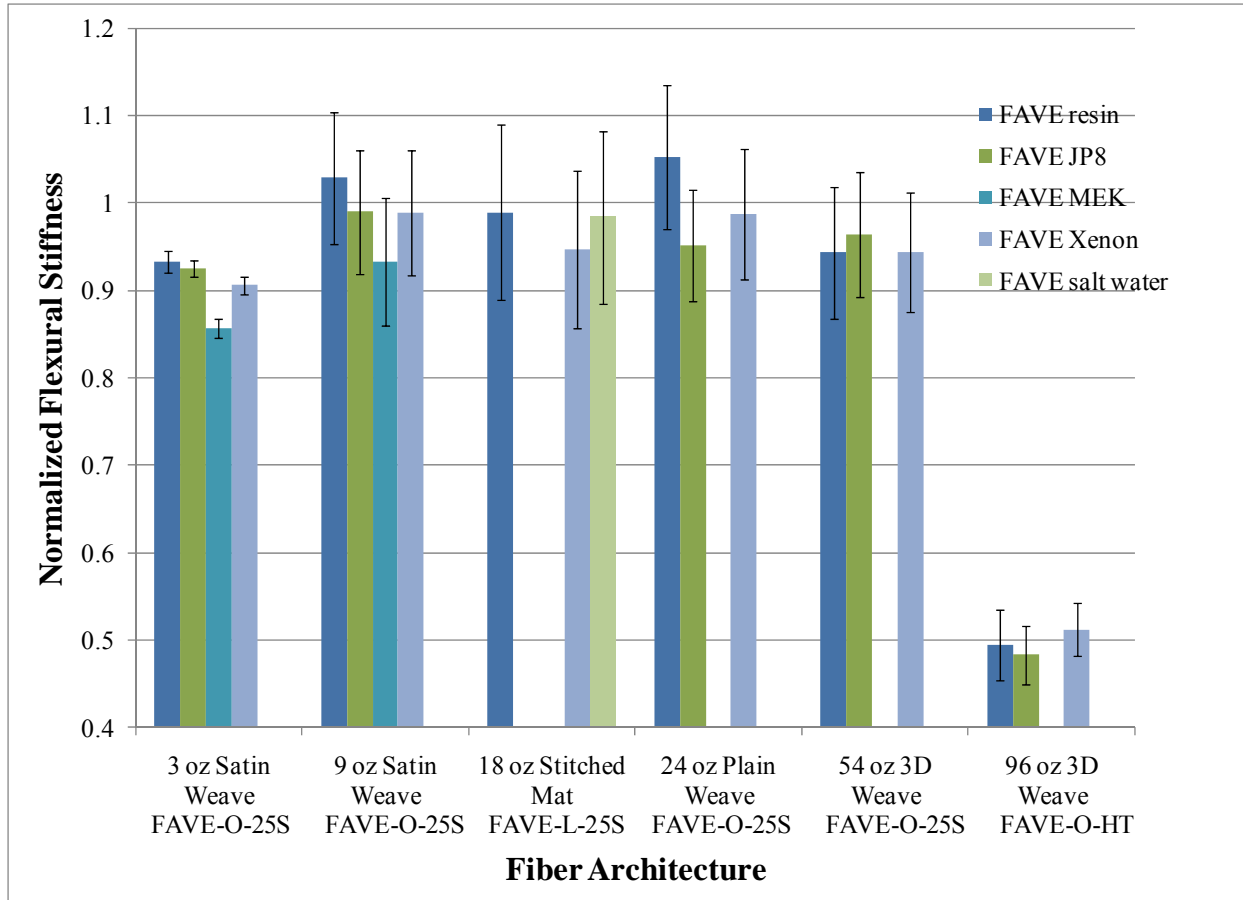


Figure 5. Normalized flexural stiffness of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.

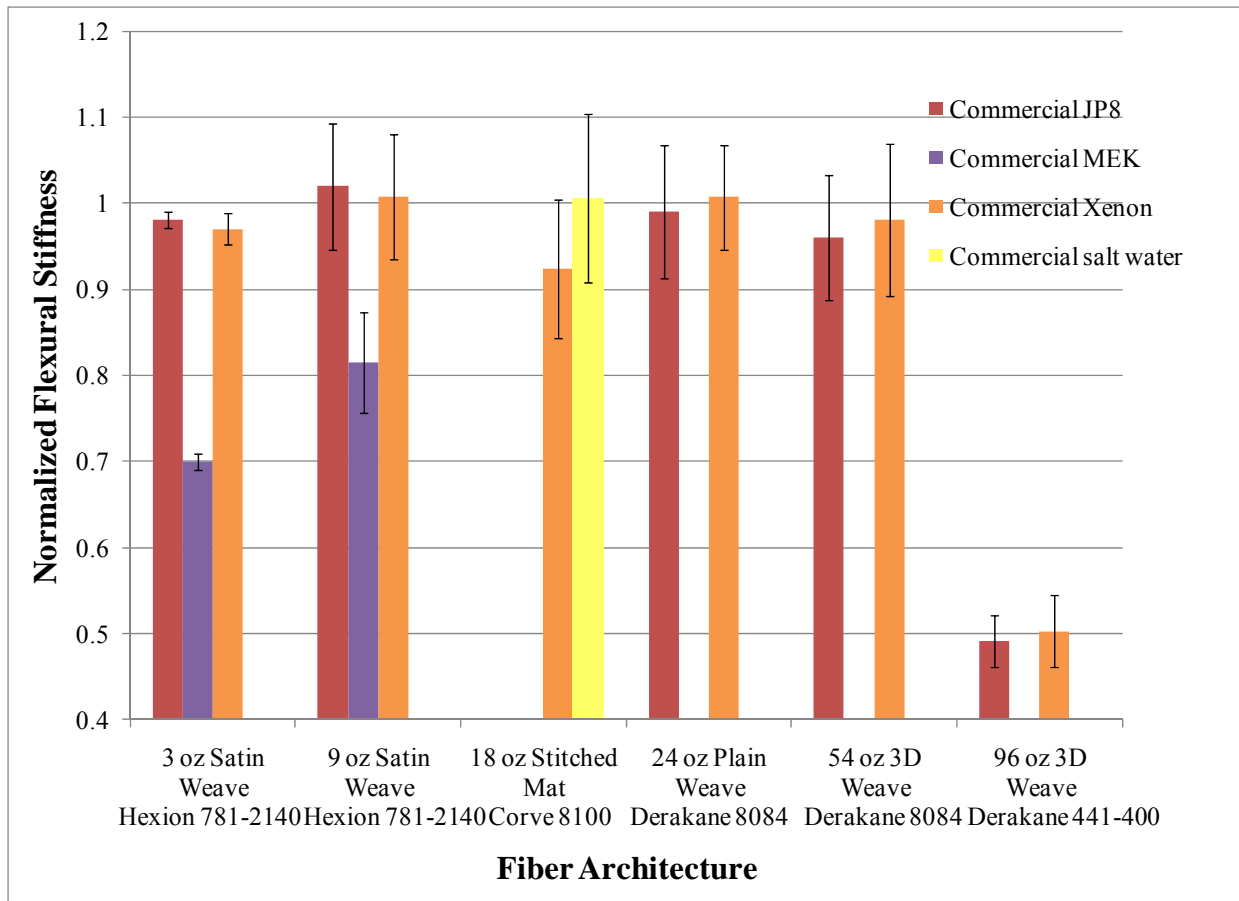


Figure 6. Normalized flexural stiffness of aged commercial resin composites vs. their unaged commercial composite counterparts.

The effect of commercially available resin with higher styrene content vs. FAVE resin with lower styrene content on the flexural properties is difficult to determine from the data. Before weathering, most composites with the same fiber architecture but different resin systems performed very similar to each other within experimental error. However, there is a distinct drop in the 3-oz satin weave flexural stiffness, which may indicate that the Hexion 781-2140 with higher styrene content is forming more networks within the polymer matrix, increasing the overall composite flexural rigidity; however, this effect is not observed in the 9-oz data. Also, the 96-oz 3-D weave flexural properties showed a distinct drop between Derakane 441-400 and FAVE-O-HT. These data, however, are most likely spurious due to the explanation already presented regarding the 3-D weave sample thicknesses.

The Army composites were subjected to JP8 exposure and the Navy and Air Force composites subjected to simulated saltwater and MEK exposure, respectively. All composites were subjected to xenon weathering, which consisted of accelerated simulated sunlight exposure for 61 days. The Army composites were immersed in JP8 for 1 week and showed no appreciable effect on flexural strength or stiffness, except for the 96-oz composite, for both commercial vinyl

ester resins and FAVE resins. The Navy composites were subjected to simulated saltwater exposure for 1 month. No appreciable effect was observed on the flexural strength or stiffness except for the flexural strength of 18-oz FAVE-L-25S, which was within experimental error. The notable exception here occurred for the Air Force composites that were exposed to MEK. The significant drop in flexural properties was due to the MEK plasticizing the polymer network and reducing overall properties for composites fabricated using the commercial resins and to a lesser extent for composites fabricated using the FAVE resins.

3.2 Short Beam Shear

SBS testing was conducted on all composites, with results presented in figures 7 and 8. The results of the SBS testing appear to show much more scatter in the data than the flexural testing. Possible explanations included a reduced sample set for each composite (no sample set was larger than seven samples), the small size of the samples ($25 \times 4 \times 6$ mm) that may have contributed to error estimates in the required span, and due to the small sample size, localized fiber architecture effects may have affected the observed strength. Regardless of the

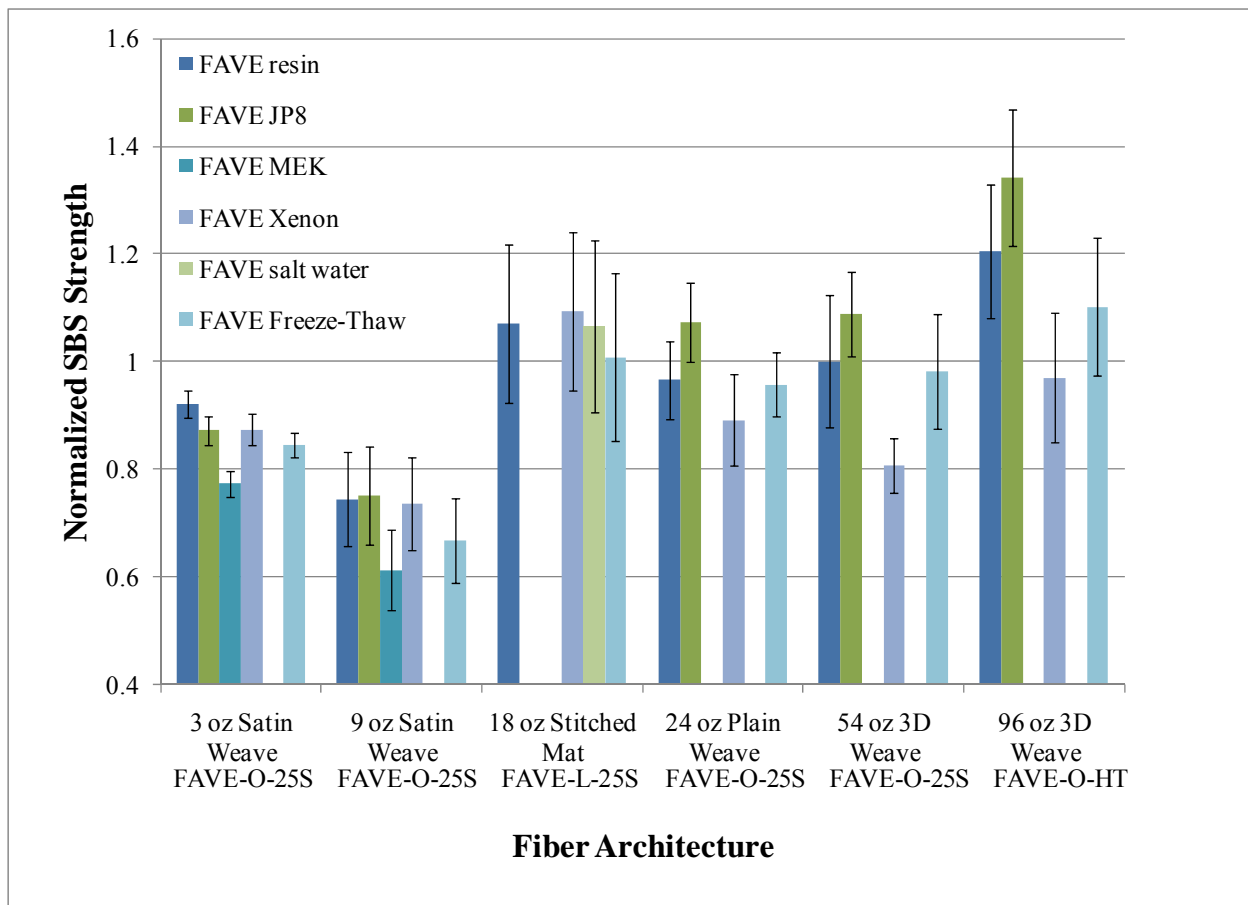


Figure 7. Normalized SBS strength of FAVE composites (unaged and aged) vs. their unaged commercial resin composite counterparts.

explanation, such scatter is often seen in SBS data sets, and it is understood that the SBS strength is just an easily obtained metric for estimating a mechanical response of a material. That said, the FAVE resin composites did appear to perform slightly better overall than the commercial vinyl ester resins with the Air Force composites, with the 3- and 9-oz satin weave being the exception.

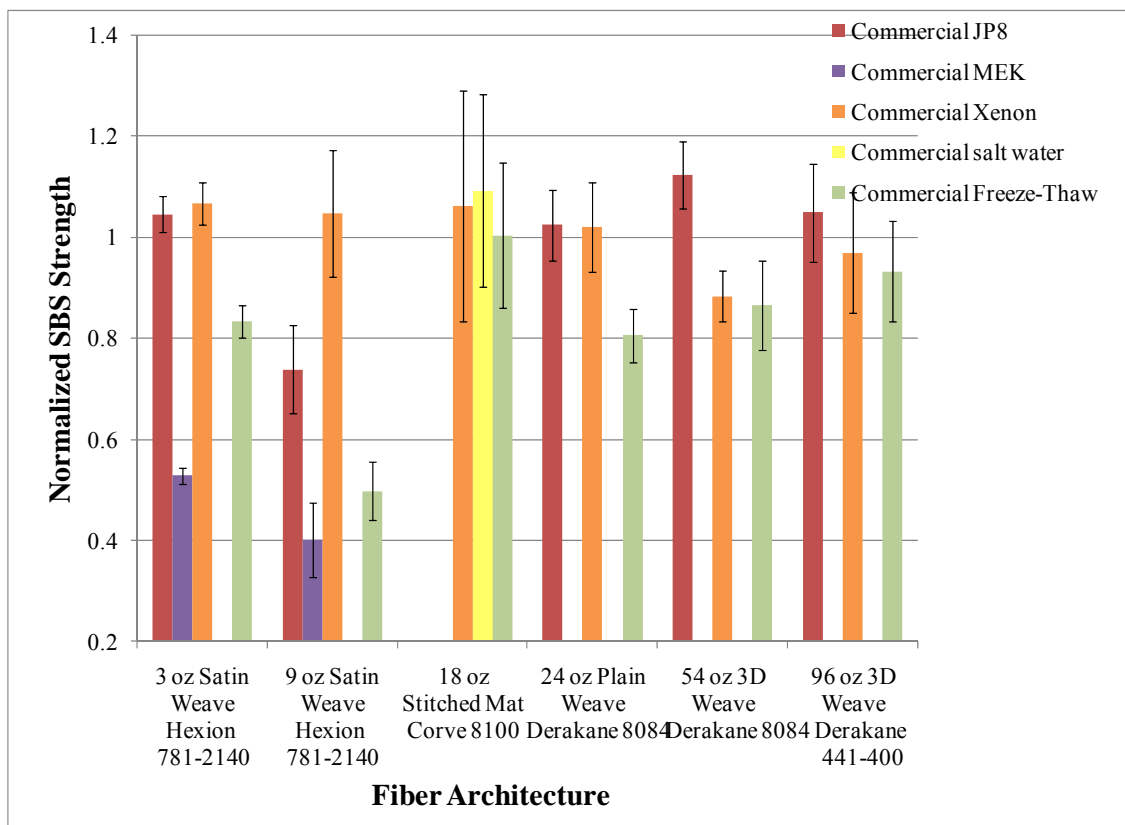


Figure 8. Normalized SBS strength of aged commercial resin composites versus their unaged commercial composite counterparts

Given the scatter in the SBS data, it is difficult to identify any possible trends due to the environmental and chemical aging exposure. The JP8 exposure for most composites did not seem to have an effect on the SBS strength compared to the baseline except for the 9-oz Hexion composite. The behavior of the 9-oz Hexion samples is odd considering that the 9-oz FAVE-O-25S SBS strength seemed unaffected by the other types of aging. The increases in SBS strength observed in the Army composites (24-oz PW and 54-oz 3-D weave) are probably within experimental error, and the 96-oz data are probably suspect for reasons discussed earlier. Most composites also did not show any effect due to xenon weathering except the 54-oz composites. The most notable trend observed in the SBS strength data was in the freeze-thaw-soak. All composites demonstrated a drop in SBS response under repeated freeze-thaw-soak cycles. The predominate mechanism here is matrix cracking, which is caused by water sorption and water

expansion during freezing, creating and propagating cracks in the polymer matrix. SBS testing was also conducted on the Navy and Air Force composites. The simulated saltwater exposure had little effect on the SBS strength of the Navy composites. However, the MEK soak significantly reduced the SBS strength of the highly styrenated resin composite, Hexion 781-2140 and Corve 8100, and moderately decreased the strength of the FAVE composites for both the 3- and 9-oz satin weave composites, as shown in figure 8. Again, the MEK exposure plasticized the polymer matrix, causing a decrease in mechanical properties.

3.3 Wet and Dry Glass Transition Temperature

Wet and dry glass transition temperatures for the polymer matrices were measured for the unaged baseline in figure 9 and dry T_g compared to the baseline for a few select types of aging, as presented in figure 10. The dry and wet T_g values of all composites are presented in figure 8. Overall, the more styrenated commercially available resins had higher T_g values than the FAVE resins with lower styrene content but were still within about 15 °C. The notable exception was the FAVE-O-HT resin, which is a novolac vinyl ester specifically formulated to have a higher T_g . The wet T_g measurements showed a characteristic drop usually observed in water-saturated polymer resins, which was recovered under a second heating run. Figures 9 and 10 have no standard deviation because no sample set for the glass transition data was collected due to the availability of virgin DMA samples and limited experimental time on the DMA unit. However, previous DMA results for the pure resin samples confirm these trends (15).

Dry glass transition temperatures for the baseline (no aging) and for JP8 exposure, freeze-thaw-soak exposure, and MEK exposure are shown in figure 10. Exposure to JP8 appeared to give a slight boost to the T_g of all composites tested, although the reason or mechanism is unknown. A mild decrease was observed with the freeze-thaw-soak exposure, which was consistent across all the resin systems. The most significant result from figure 10 is the decrease in T_g displayed by the two styrenated resins subject to MEK exposure, Hexion 781-2140 and Corve 8100, while FAVE-O-25S composites are unaffected. This demonstrates that the decrease observed in mechanical properties and T_g is due to the MEK plasticizing the polymer network and not to removing unreacted styrene, which would likely result in a T_g increase.

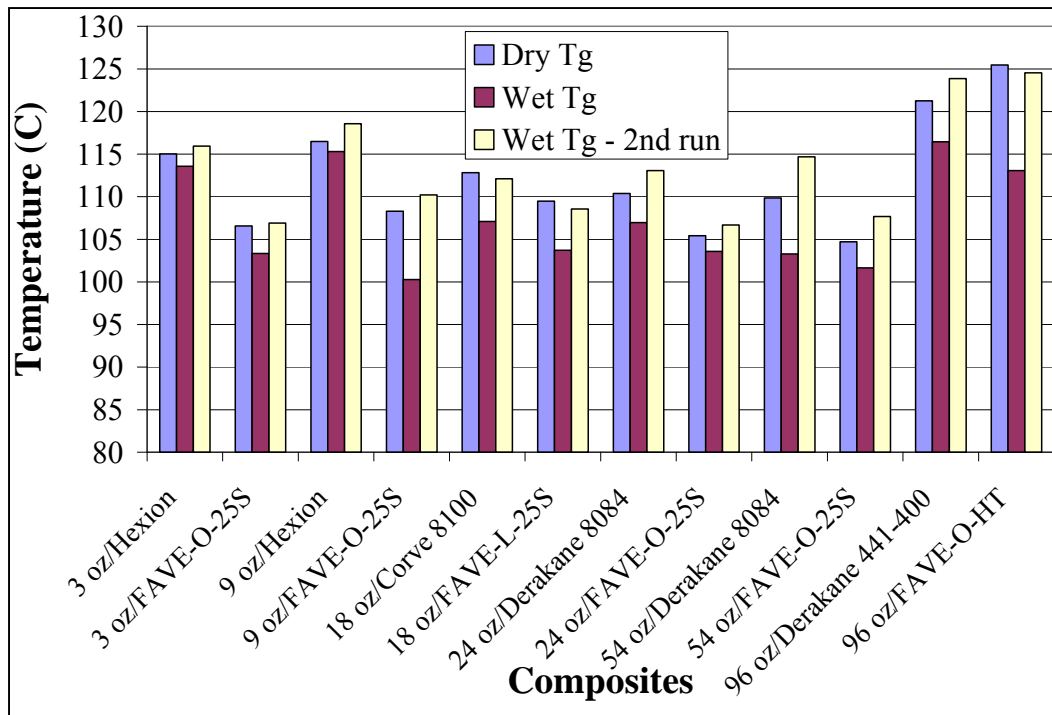


Figure 9. Dry and wet glass transition temperatures for commercial and FAVE composites.

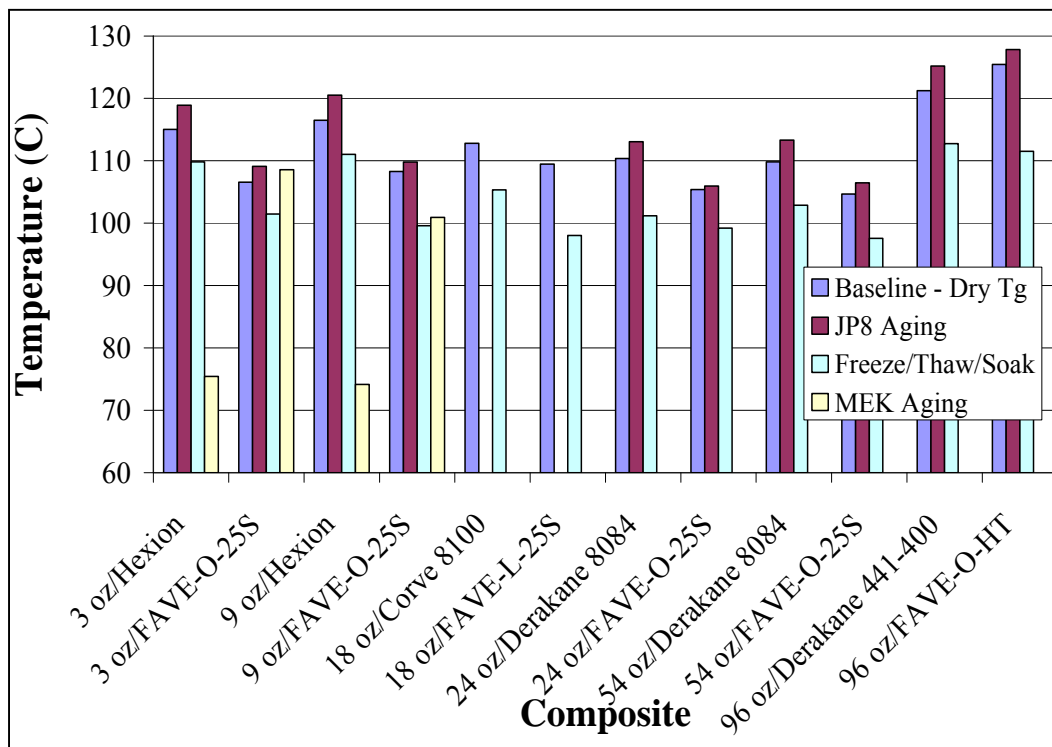


Figure 10. Glass transition temperatures (dry) for commercial and FAVE composites: baseline (no aging), JP8 aging, freeze-thaw-soak aging, and MEK aging.

4. Conclusions

A survey of the response of mechanical and thermal properties of commercially available vinyl ester resin and FAVE resin composites to various types of aging is presented in this study. The goal was to evaluate any potential negative effects on the composite properties due to aging or exposure and demonstrate that lower styrene content fatty-acid vinyl ester resins could perform as well as their higher styrene content, commercially available counterparts.

Overall, the FAVE composites performed as well as the commercially available vinyl ester resin composites. Although the resin systems with higher styrene content had better thermal properties (higher T_g values), the FAVE composites whose matrices had lower styrene content displayed equivalent mechanical properties and resistance to aging and exposure. The most notable difference occurred with MEK exposure of the Air Force composites, where in contrast, the FAVE composites retained their thermal and mechanical properties after exposure.

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